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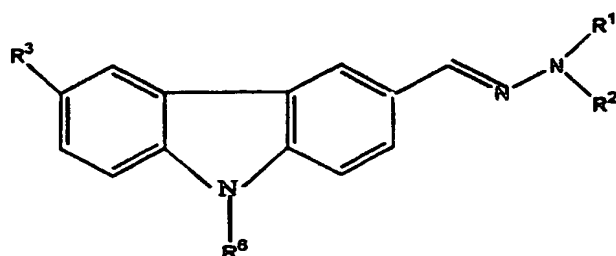
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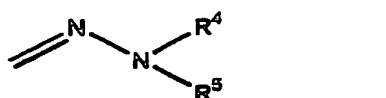
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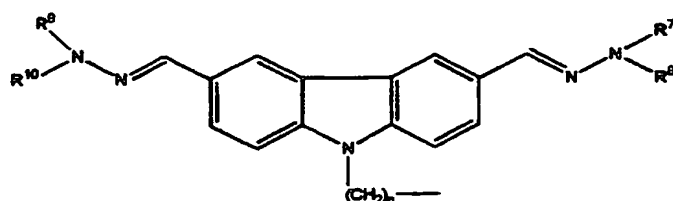
(54) Title: ORGANOPHOTORECEPTORS FOR ELECTROPHOTOGRAPHY COMPRISING HYDRAZONE CHARGE
TRANSPORT COMPOUNDS



(1)



(i)



(ii)

(57) Abstract: The invention features an organic photoreceptor that includes: (a) a charge transport compound having formula (1) where R¹ and R², independently, are hydrogen, an alkyl group (e.g., a C₁₋₆ alkyl group), or an aryl group (e.g., a phenyl or naphthyl group); R³ is hydrogen or a hydrazone group having formula (i); R⁴ and R⁵, independently, are hydrogen, an alkyl group (e.g., a C₁₋₆ alkyl group), or an aryl group (e.g., a phenyl or naphthyl group); R⁶ is an aryl group (e.g., a phenyl or naphthyl group); straight or branched alkyl group having at least 7 carbon atoms; a group having the formula -(CH₂)_n-Ar where n is at least 3, Ar represents an aryl group (e.g., a phenyl or naphthyl group), and one or more methylene groups is optionally substituted with a hetero atom; or a carbazole group having formula (ii) where R⁷, R⁸, R⁹, and R¹⁰, independently, are hydrogen, an alkyl group (e.g., a C₁₋₆ alkyl group), or an aryl group (e.g., a phenyl or naphthyl group); n is at least 3; and one or more methylene groups is optionally substituted with a heteroatom; (b) a charge generating compound; and (c) an electroconductive substrate.



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ORGANOPHOTORECEPTORS FOR ELECTROPHOTOGRAPHY COMPRISING HYDRAZONE CHARGE
TRANSPORT COMPOUNDS

BACKGROUND

This invention relates to organic photoreceptors suitable for use in electrophotography.

In electrophotography, a photoreceptor in the form of a plate, belt, or drum
5 having an electrically insulating photoconductive element on an electrically
conductive substrate is imaged by first uniformly electrostatically charging the
surface of the photoconductive layer, and then exposing the charged surface to a
pattern of light. The light exposure selectively dissipates the charge in the
illuminated areas, thereby forming a pattern of charged and discharged areas. A
10 liquid or solid toner is then deposited in either the charged or discharged areas to
create a toned image on the surface of the photoconductive layer. The resulting
visible toner image can be transferred to a suitable receiving surface such as paper.
The imaging process can be repeated many times.

Both single layer and multilayer photoconductive elements have been used.
15 In the single layer embodiment, a charge transport material and a charge generating
material are combined with a polymeric binder and then deposited on the electrically
conductive substrate. In the multilayer embodiment, the charge transport material
and charge generating material are in the form of separate layers, each of which can
optionally be combined with a polymeric binder, deposited on the electrically
20 conductive substrate. Two arrangements are possible. In one arrangement (the "dual
layer" arrangement), the charge generating layer is deposited on the electrically
conductive substrate and the charge transport layer is deposited on top of the charge
generating layer. In an alternate arrangement (the "inverted dual layer" arrangement),
the order of the charge transport layer and charge generating layer is reversed.

25 In both the single and multilayer photoconductive elements, the purpose of
the charge generating material is to generate charge carriers (i.e., holes and electrons)
upon exposure to light. The purpose of the charge transport material is to accept

these charge carriers and transport them through the charge transport layer in order to discharge a surface charge on the photoconductive element.

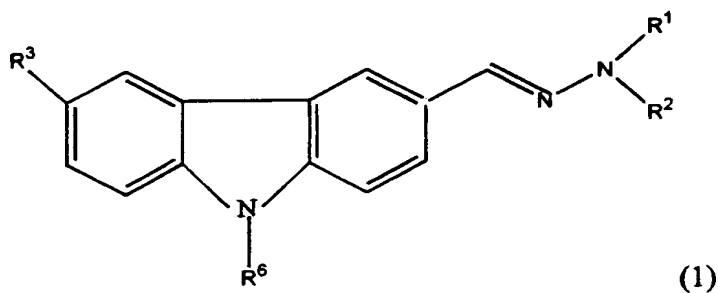
To produce high quality images, particularly after multiple cycles, it is desirable for the charge transport material to form a homogeneous solution with the polymeric binder and remain in solution. In addition, it is desirable to maximize the amount of charge which the charge transport material can accept (indicated by a parameter known as the acceptance voltage or " V_{acc} "), and to minimize retention of that charge upon discharge (indicated by a parameter known as the residual voltage or " V_{res} ").

Liquid toners generally produce superior images compared to dry toners. However, liquid toners also can facilitate stress crazing in the photoconductive element. Stress crazing, in turn, leads to printing defects such as increased background. It also degrades the photoreceptor, thereby shortening its useful lifetime. The problem is particularly acute when the photoreceptor is in the form of a flexible belt included in a compact imaging machine that employs small diameter support rollers (e.g., having diameters no greater than about 40 mm) confined within a small space. Such an arrangement places significant mechanical stress on the photoreceptor, and can lead to degradation and low quality images.

SUMMARY

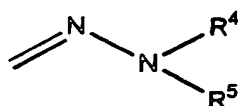
In a first aspect, the invention features an organic photoreceptor that includes:

- (a) a charge transport compound having the formula



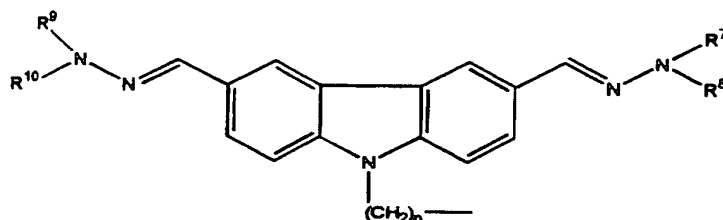
where R^1 and R^2 , independently, are hydrogen, an alkyl group (e.g., a C_1 - C_6 alkyl group), or an aryl group (e.g., a phenyl or naphthyl group);

R^3 is hydrogen or a hydrazone group having the formula



5 R^4 and R^5 , independently, are hydrogen, an alkyl group (e.g., a C_1 - C_6 alkyl group), or an aryl group (e.g., a phenyl or naphthyl group);

R^6 is an aryl group (e.g., a phenyl or naphthyl group); straight or branched alkyl group having at least 7 carbon atoms; a group having the formula $-(CH_2)_n-$ Ar where n is at least 3, Ar represents an aryl group (e.g., a phenyl or naphthyl group), and one or more methylene groups is optionally substituted with a hetero atom; or a carbazole group having the formula



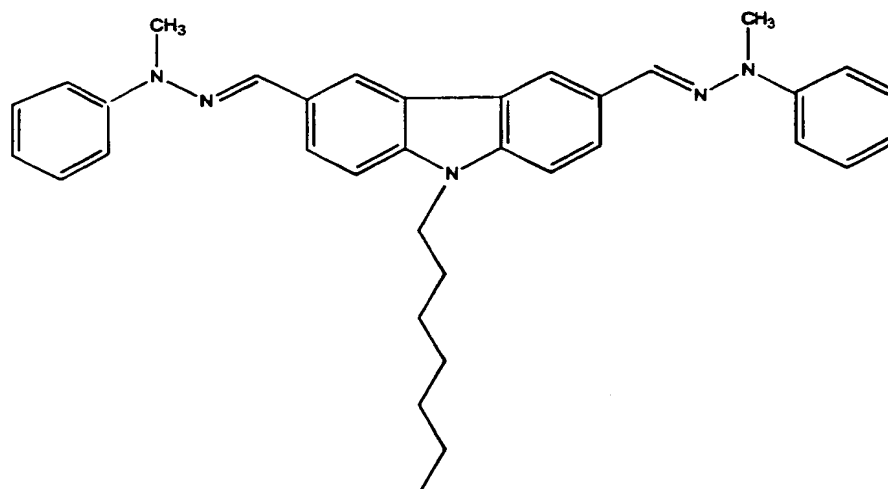
15 where R^7 , R^8 , R^9 , and R^{10} , independently, are hydrogen, an alkyl group (e.g., a C_1 - C_6 alkyl group), or an aryl group (e.g., a phenyl or naphthyl group); n is at least 3; and one or more methylene groups is optionally substituted with a heteroatom;

- (b) a charge generating compound; and
- (c) an electroconductive substrate.

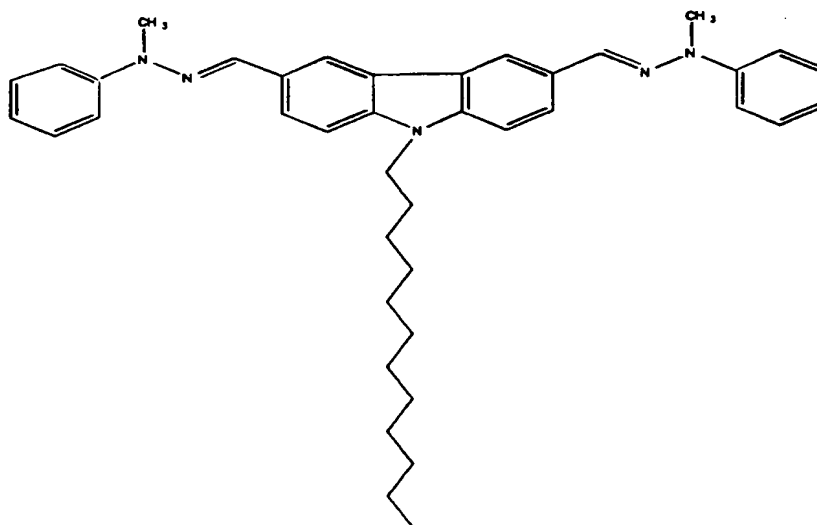
20 The organic photoreceptor may be provided in the form of a flexible belt. In one embodiment, the organic photoreceptor includes: (a) a charge transport layer comprising at least one of the charge transport compounds and a polymeric binder; (b) a charge generating layer comprising the charge generating compound and a polymeric binder; and (c) the electroconductive substrate. The charge

transport layer preferably has a glass transition temperature of at least about 80°C. In one embodiment, the charge transport layer includes two of the charge transport compounds in a ratio with one another of about 9:1 to about 1:1. The charge transport layer may be intermediate the charge generating layer and the electroconductive substrate. Alternatively, the charge generating layer may be intermediate the charge transport layer and the electroconductive substrate.

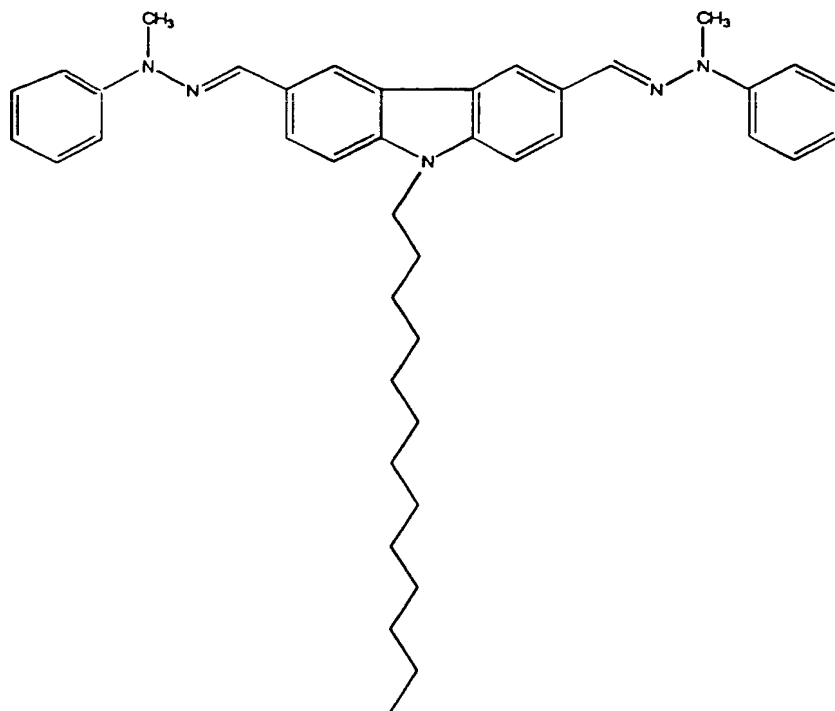
In one preferred embodiment, a charge transport compound is selected in which R³ is a hydrazone group, R⁴ is a methyl group, and R⁵ is a phenyl group. Specific examples of suitable charge transport compounds have the following formulae:



; (2)

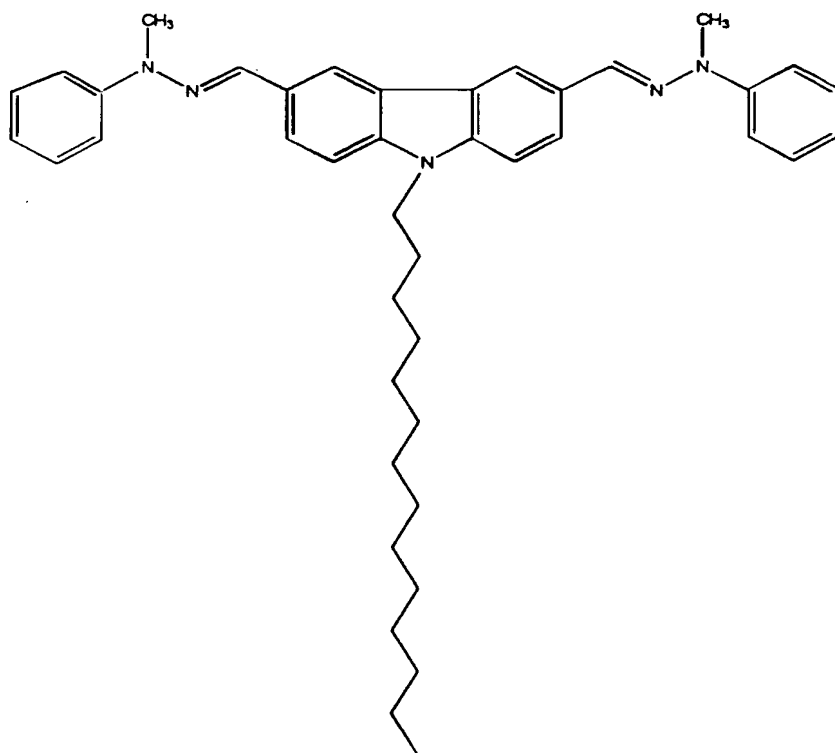


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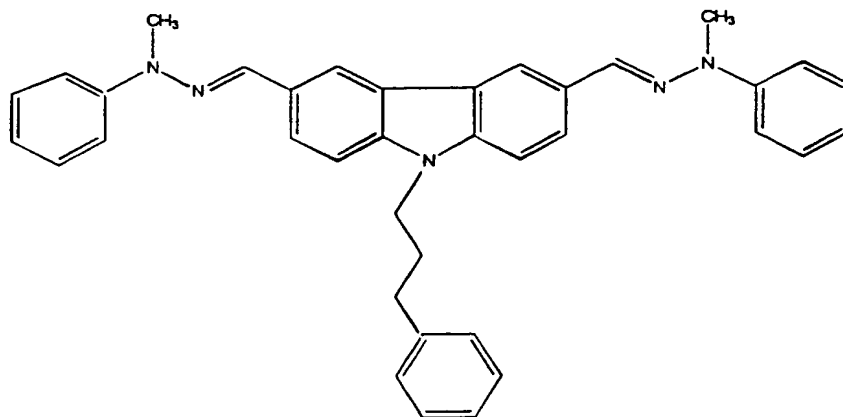
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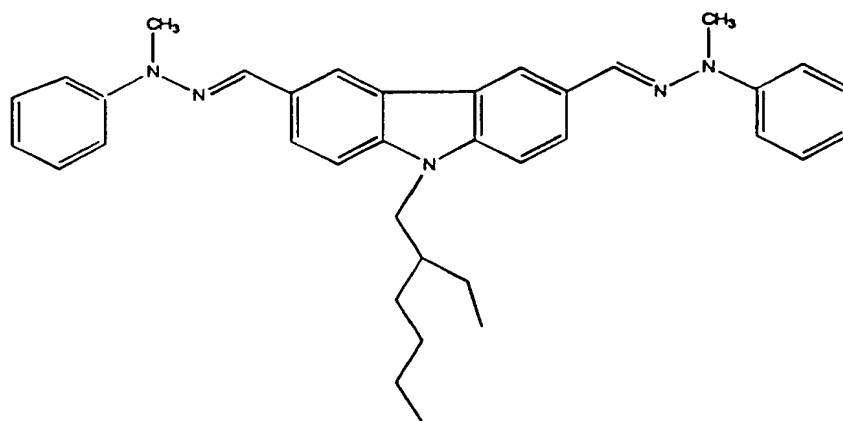


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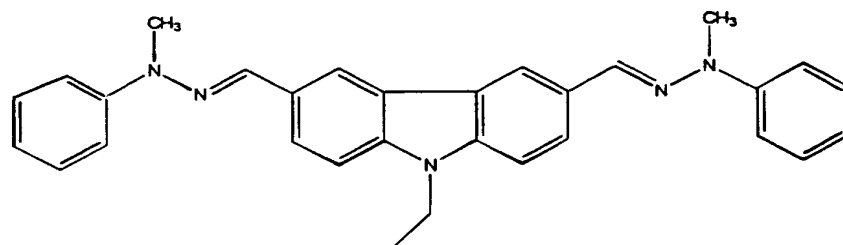
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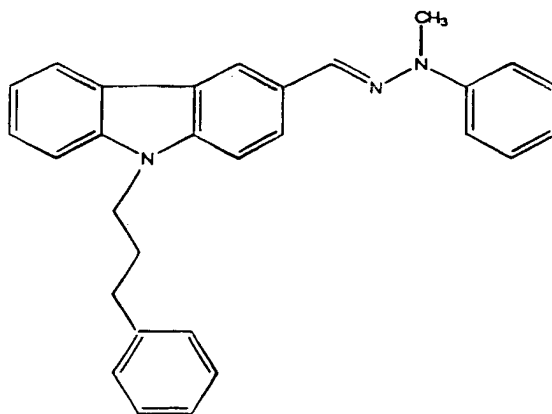
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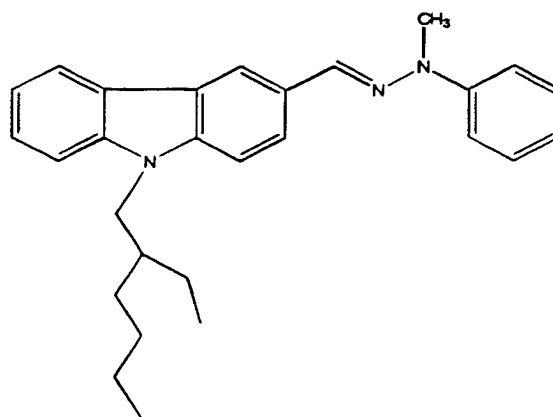
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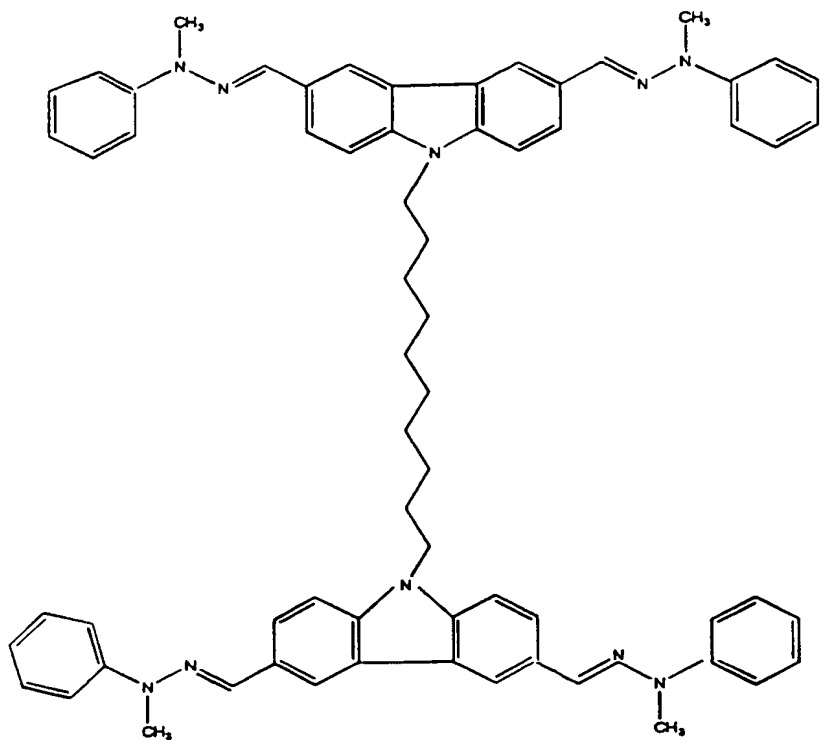
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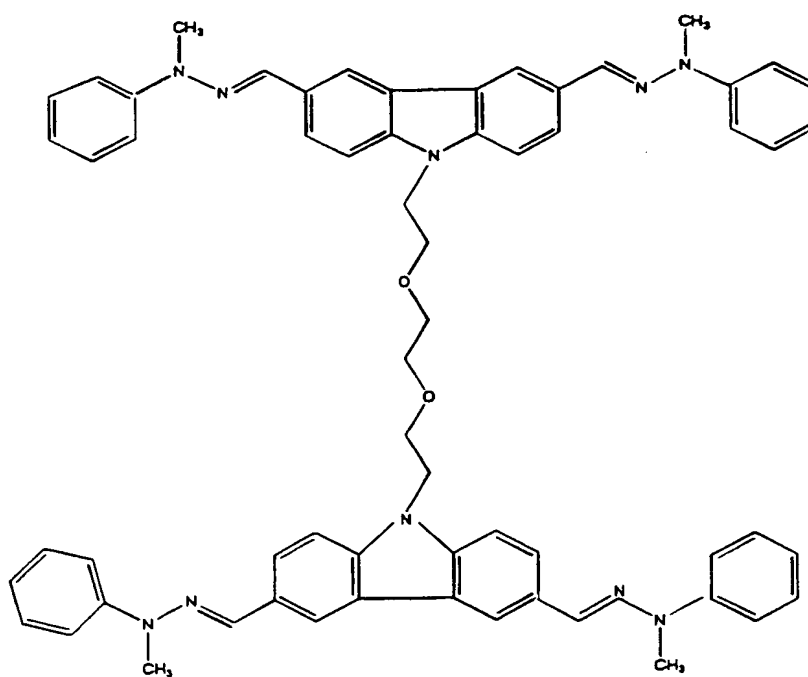
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The charge transport compounds may be used alone or in combination with each other. The invention also features the charge transport compounds themselves.

5 In a second aspect, the invention features an electrophotographic imaging apparatus that includes (a) a plurality of support rollers and (b) the above-described organic photoreceptor in the form of a flexible belt supported by the support rollers. Preferably, at least one of the support rollers has a diameter no greater than about 40 mm. The apparatus preferably further includes a liquid toner dispenser.

10 In a third aspect, the invention features an electrophotographic imaging process that includes (a) applying an electrical charge to a surface of the above-described organic photoreceptor; (b) imagewise exposing the surface of the organic photoreceptor to radiation to dissipate charge in selected areas and thereby form a pattern of charged and discharged areas on the surface; (c) contacting the surface with a liquid toner that includes a dispersion of colorant particles in an organic
15 liquid to create a toned image; and (d) transferring the toned image to a substrate.

In a preferred embodiment, the organic photoreceptor is in the form of a flexible belt, e.g., a flexible belt supported by a plurality of support rollers, at least one of which has a diameter no greater than about 40 mm.

20 The invention provides organic photoreceptors featuring a combination of good mechanical properties and electrostatic properties. These photoreceptors can be used successfully with liquid toners to produce high quality images even when subjected to significant mechanical stresses encountered when the photoreceptor is in the form of a flexible belt supported by a plurality of small diameter rollers. The high quality of the images is maintained after repeated cycling.

25 Other features and advantages of the invention will be apparent from the following description of the preferred embodiments thereof, and from the claims.

DETAILED DESCRIPTION

The invention features organic photoreceptors that include charge transport compounds having the formulae set forth in the Summary of the Invention, above.
30 The charge transport compounds are aryl hydrazone-functional carbazoles. They are preferably prepared via N-alkylation of a carbazole, followed by a Vielsmayer

reaction to form an aldehyde group on the carbazole molecule, and then reaction of the aldehyde with a hydrazine to form the final hydrazone product.

In some cases, it may be desirable to include two or more charge transport compounds in a single charge transport layer in order to increase solubility in the solvent used to prepare the layer. For example, a 1:1 mixture by weight of two charge transport compounds may be more soluble in a solvent such as tetrahydrofuran than each one individually at the same concentration. Increased solubility results in layers having improved uniformity and transparency, as well as improved electrostatic properties. Preferably, two charge transport compounds are utilized in a ratio with one another of about 9:1 to about 1:1.

The organic photoreceptor may be in the form of a plate, drum, or belt, with the novel charge transport compounds being particularly useful in the case of flexible belts. The photoreceptor may include a conductive substrate and a photoconductive element in the form of a single layer that includes both the charge transport compound, the charge generating compound, and separate polymeric binder. Preferably, however, the photoreceptor includes a conductive substrate and a photoconductive element that is a bilayer construction featuring a charge generating layer and a separate charge transport layer. The charge generating layer may be located intermediate the conductive substrate and the charge transport layer. Alternatively, the photoconductive element may be an inverted construction in which the charge transport layer is intermediate the conductive substrate and the charge generating layer.

The photoreceptors are suitable for use in an imaging process with either dry or liquid toner development. Liquid toner development is generally preferred because it offers the advantages of providing higher resolution images and requiring lower energy for image fixing compared to dry toners. Examples of useful liquid toners are well-known. They typically include a colorant, a resin binder, a charge director, and a carrier liquid. A preferred resin to pigment ratio is 2:1 to 10:1, more preferably 4:1 to 8:1. Typically, the colorant, resin, and the charge director form the toner particles.

The photoreceptors are particularly useful in a compact imaging apparatus where the photoreceptor is wound around several small diameter rollers (e.g., having diameters no greater than about 40 mm). A number of apparatus designs may be employed, including, for example, the apparatus designs disclosed in U.S. 5,650,253 and U.S. 5,659,851.

The charge generating compound is a material which is capable of absorbing light to generate charge carriers, such as a dyestuff or a pigment. One example of a suitable charge generating compound is a metal-free phthalocyanine pigment (e.g., Progen 1 x-form metal-free phthalocyanine pigment from Zeneca, Inc.). Also suitable are Y-form metal-free phthalocyanine pigments.

The binder is capable of dispersing or dissolving the charge transport compound (in the case of the charge transport layer) and the charge generating compound (in the case of the charge generating layer). Examples of suitable binders for both the charge generating layer and charge transport layer include styrenebutadiene copolymers, modified acrylic polymers, vinyl acetate polymers, styrene-alkyd resins, soya-alkyl resins, polyvinyl chloride, polyvinylidene chloride, acrylonitrile, polycarbonate, polyacrylic and methacrylic esters, polystyrene, polyesters, and combinations thereof. Examples of suitable polycarbonate binders include aryl polycarbonates such as poly(4,4-dihydroxy-diphenyl-1,1-cyclohexane) ("Polycarbonate Z") and poly(Bisphenol A carbonate co-4,4'(3,3,5-trimethyl cyclohexylidene diphenol)). Another example of a useful binder is polyvinyl butyral.

Other layers that may be included in the photoreceptor include, for example, barrier layers and release layers. Examples of suitable barrier layers include crosslinkable siloxanol-colloidal silica hybrids (as disclosed, e.g., in U.S. Patent Nos. 4,439,509; 4,606,934; 4,595,602; and 4,923,775); a coating formed from a dispersion of hydroxylated silsesquioxane and colloidal silica in an alcohol medium (as disclosed, e.g., in U.S. Patent No. 4,565,760); a polymer resulting from a mixture of polyvinyl alcohol with methyl vinyl ether/maleic anhydride copolymer; and polyvinyl butyral crosslinked with a copolymer of maleic anhydride and methylvinyl ether (commercially available under the trade designation GANTREZ AN169) containing about 30% silica. Examples of suitable release layers include fluorinated polymers,

siloxane polymers, silanes, polyethylene, and polypropylene, with crosslinked silicone polymers being preferred.

The invention will now be described further by way of the following examples.

EXAMPLES

A. Synthesis

Charge transport compounds were synthesized as follows. The number associated with each compound refers to the number of the chemical formula set forth in the Summary of the Invention, above.

Compound (2)

To a 1-liter 3-neck round bottom flask equipped with reflux condenser and mechanical stirrer were added 88.69 g carbazole (0.53 mol), 100 g 1-bromoheptane (0.56 mol), 6.00 g benzyltriethyl ammonium chloride (0.026 mol) and 400 ml of toluene. The mixture was stirred at room temperature for 0.5 hr., followed by the addition of an aqueous solution of NaOH (prepared by dissolving 100 g of NaOH in 100 g water). The mixture was refluxed for 5 hr. and cooled to room temperature. The organic phase was separated and washed repeatedly with water until the pH of the washing water was neutral. The organic phase was dried over Mg_2SO_4 , filtered, and evaporated to dryness to obtain 126 g of brown liquid (89% yield). 1H -NMR and IR spectra were in agreement with the structure of N-heptylcarbazole.

To a 1-liter, 3-neck round bottom flask equipped with mechanical stirrer, thermometer, and addition funnel, was added 271 ml DMF (3.5 mol). The contents were cooled in a salt/ice bath. When the temperature inside the flask reached 0°C, 326 ml of $POCl_3$ (3.5 mol) was slowly added. During the addition of $POCl_3$, the temperature inside the flask was not allowed to rise above 5°C. After the addition of $POCl_3$ was completed, the reaction mixture was allowed to warm to room temperature. 126 g of N-heptylcarbazole was then added and the flask was heated to 90°C for 24 hr. using a heating mantle. The reaction mixture was cooled to room temperature and the solution was added slowly to a 4.5 liter beaker containing a solution of 820 g sodium acetate dissolved in 2 liters of water. The

beaker was cooled in an ice bath and stirred for 3 hr. The brownish solid obtained was filtered and washed repeatedly with water, followed by a small amount of ethanol (50 ml). The resulting product was recrystallized once from toluene using activated charcoal and dried under vacuum in an oven heated at 70°C for 6 hr to
5 obtain 80 g (51% yield) of N-heptyl-3,6-diformyl-carbazole. ¹H-NMR and IR spectra confirmed the presence of N-heptyl-3,6-diformyl-carbazole.

To a 250 ml 3-neck round bottom flask equipped with reflux condenser and mechanical stirrer were added 9.63 g (0.03 mol) of N-heptyl-3,6-diformylcarbazole and 100 ml toluene. Heating was applied until all solid entered into solution, then
10 8 drops of concentrated HCl were added, followed by the addition of a solution of 7.7 g of N-methyl-N-phenylhydrazine (0.063 mol) in 25 ml toluene. The flask was heated under reflux for 5 hr, during which a solid was formed. The flask was cooled to room temperature and the solid was filtered off, washed with toluene and ethanol, and dried in an oven at 70°C under vacuum for 6 hr. The product was
15 recrystallized three times from toluene using activated charcoal in all three recrystallizations. Celite was also used in the third recrystallization. The product was dried at 70°C under vacuum for 6 hr to obtain 10 g of Compound (2) as a light yellow solid (63% yield). ¹H-NMR and IR were in agreement with the proposed structure.

20 Compound (3)

N-dodecyl carbazole was prepared from carbazole (66 g, 0.40 mol), 1-bromododecane (100 g, 0.41 mol), benzyltriethyl ammonium chloride (4.48 g, 0.02 mol), toluene (400 ml), and sodium hydroxide (200 g of 50% aqueous solution) according to the procedure described for Compound (2). The product was obtained
25 as 115 g of brown liquid (87% yield). ¹H-NMR and IR confirmed the structure to be N-dodecylcarbazole.

N-dodecyl-3,6-diformyl carbazole was prepared from DMF (186 ml, 2.4 mol), POCl₃ (224 ml, 2.4 mol), and N-dodecylcarbazole (115 g, 0.34 mol), according to the procedure described for Compound (2). The product was recrystallized once
30 from THF/water to yield 100 g of a brown solid (75% yield). ¹H-NMR and IR confirmed the structure to be N-dodecyl-3,6-diformylcarbazole.

Compound (3) was prepared from N-dodecyl-3,6-diformyl-carbazole (11.76 g, 0.03 mol), N-methyl-N-phenylhydrazine (7.7 g, 0.063 mol), and 8 drops of conc. HCl according to the procedure described for Compound (2). The solid was recrystallized 3 times from toluene using activated charcoal. Celite was also used in the third recrystallization. 11 g (61% yield) of Compound (3) were obtained. ¹H-NMR and IR spectra were in agreement with the proposed structure.

Compound (4)

N-tridecylcarbazole was prepared from carbazole (62.43 g, 0.37 mol), 1-bromotridecane (100 g, 0.38 mol), benzyltriethyl ammonium chloride (4.24 g, 0.018 mol), toluene (400 ml), and 50% aqueous NaOH (200 g) according to the procedure described for Compound (2). The product was obtained as 120 g of brown liquid (96% yield). ¹H-NMR and IR confirmed the structure to be N-tridecylcarbazole.

N-tridecyl-3,6-diformyl carbazole was prepared from DMF (186 ml, 2.4 mol), POCl₃ (224 ml, 2.4 mol), and N-tridecylcarbazole (120 g, 0.34 mol) according to the procedure described for Compound (2). The product was recrystallized from THF/water to yield 130 g (84% yield) of purified product. ¹H-NMR and IR spectra confirmed the structure to be N-tridecyl-3,6-diformylcarbazole.

Compound (4) was prepared from N-tridecyl-3,6-diformyl-carbazole (130 g, 0.32 mol), N-methyl-N-phenylhydrazine (82.15 g, 0.67 mol), and concentrated HCl (5 ml) according to the procedure described for Compound (2). The product was recrystallized 3 times from toluene to yield 100 g (50% yield) of Compound (4). ¹H-NMR and IR spectra were in agreement with the structure of Compound (4).

Compound (5)

N-tetradecylcarbazole was prepared from carbazole (59.27 g, 0.35 mol), 1-bromotetradecane (100 g, 0.36 mol), benzyltriethyl ammonium chloride (4.00 g, 0.018 mol), 50% aqueous NaOH (200 g), and toluene (400 ml) according to the procedure described for Compound (2). The product was obtained as 120 g of a brown liquid (93% yield). Upon standing at room temperature overnight, the liquid solidified. ¹H-NMR and IR spectra confirmed the structure to be N-tetradecylcarbazole.

N-tetradecyl-3,6-diformylcarbazole was prepared from DMF (186 ml, 2.4 mol), POCl₃ (224 ml, 2.4 mol), and N-tetradecylcarbazole (120 g, 0.33 mol) according to the procedure described for Compound (2). 117 g of product were obtained (84% yield). ¹H-NMR and IR confirmed the structure to be N-tetradecyl-3,6-diformylcarbazole.

Compound (5) was prepared from N-tetradecyl-3,6-diformylcarbazole (117 g, 0.28 mol), N-methyl-N-phenylhydrazine (71.28 g, 0.58 mol), and concentrated HCl (5 ml) according to the procedure described for Compound (2). 85 g (49% yield) of Compound (5) were obtained. ¹H-NMR and IR spectra were in agreement with the structure of Compound (5).

Compound (6)

N-propylphenylcarbazole was prepared from carbazole (82.18 g, 0.49 mol), 1-bromo-3-phenylpropane (100 g, 0.50 mol), benzyltriethyl ammonium chloride (5.58 g, 0.025 mol), toluene (400 ml), and 50% aqueous NaOH (200 g) according to the procedure described for Compound (2). 108 g of the product was obtained as a white solid (77% yield). ¹H-NMR and IR spectra confirmed the structure to be N-propylphenylcarbazole.

N-propylphenyl-3,6-diformyl carbazole was prepared from DMF (204 ml, 2.64 mol), POCl₃ (246 ml, 2.64 mol), and N-propylphenylcarbazole (107.84 g, 0.38 mol) according to the procedure described for Compound (2). A brownish solid was obtained which was recrystallized from THF/water to yield 91.5 g (70% yield) of the product. ¹H-NMR and IR spectra confirmed the structure to be N-propylphenyl-3,6-diformylcarbazole.

Compound (6) was prepared from N-propylphenyl-3,6-diformylcarbazole (91.5 g, 0.27 mol), N-methyl-N-phenyl-hydrazine (68.66 g, 0.56 mol), concentrated HCl (5 ml), and THF (900 ml total) according to the procedure described for Compound (2). A light yellow solid was obtained which was recrystallized 3 times from toluene using activated charcoal in all recrystallizations. Celite was also used in the third recrystallization. 90 g (62% yield) of Compound (6) were obtained. ¹H-NMR and IR spectra were in agreement with the structure of Compound (6).

Compound (7)

N-2-ethylhexylcarbazole was prepared from carbazole (85.09 g, 0.51 mol), 2-ethylhexylbromide (100 g, 0.52 mol), benzyltriethyl ammonium chloride (5.78 g, 0.025 mol), toluene (400 ml), and 50% aqueous NaOH solution (200 g) according to the procedure described for Compound (2). The product was obtained as 115 g of brownish liquid (81% yield). ¹H-NMR and IR spectra confirmed the structure to be N-2-ethylhexylcarbazole.

N-2-ethylhexyl-3,6-diformyl carbazole was prepared from DMF (97 ml, 1.25 mol), POCl₃ (116.5 ml, 1.25 mol), and N-2-ethylhexylcarbazole (50 g, 0.18 mol) according to the procedure described for Compound (2). The product was obtained as 40 g of brownish liquid (66% yield). The product was used as is in the next step without any purification. ¹H-NMR and IR spectra confirmed the structure to N-2-ethylhexyl-3,6-diformyl-carbazole.

Compound (7) was prepared from N-2-ethylhexyl-3,6-diformyl-carbazole (27 g, 0.08 mol), N-methyl-N-phenylhydrazine (20.5 g, 0.17 mol), concentrated HCl (1 ml), and toluene (100 ml) according to the procedure described for Compound (2). The light yellow solid was recrystallized 3 times from toluene using activated charcoal in all three recrystallizations. Celite was also used in the third recrystallization. 25 g (56% yield) of Compound (7) were obtained. ¹H-NMR and IR spectra were in agreement with the structure of Compound (7).

Compound (8)

N-ethyl-3,6-diformylcarbazole was prepared from DMF (232 ml, 3 mol), POCl₃ (280 ml, 3.0 mol), and N-ethylcarbazole (85.6 g, 0.44 mol) according to the procedure described for Compound (2). The product was obtained as a brownish solid which was then recrystallized from THF/water to yield 88 g (80% yield) of the product. ¹H-NMR and IR spectra confirmed the structure to be N-ethyl-3,6-diformylcarbazole.

Compound (8) was prepared from N-ethyl-3,6-diformylcarbazole (86 g, 0.34 mol), N-methyl-N-phenylhydrazine (88 g, 0.72 mol), concentrated HCl (5 ml), and THF (500 ml) according to the procedure described for Compound (2). A light yellow solid was obtained which was recrystallized three times from toluene using activated charcoal in all three recrystallizations. Celite was also used

in the third recrystallization. 67 g (43% yield) of Compound (8) were obtained.

¹H-NMR and IR spectra were in agreement with the structure of Compound (8).

Compound (9)

To a 500 ml, three neck round bottom flask equipped with mechanical
5 stirrer, thermometer, and addition funnel were added N-propylphenylcarbazole
(56 g, 0.2 mol) (prepared as described in the procedure used to prepare Compound
(6)) and DMF (300 ml). The flask was placed in an ice/salt bath. When the
temperature inside the flask reached 0°C, POCl₃ (21 ml, 0.22 mol) was added
slowly by the addition funnel. The inside temperature was not allowed to rise
10 above 5°C during the addition of the POCl₃. When the addition of POCl₃ was
completed, the flask was placed on a steam bath for 2 hr. The flask was cooled to
room temperature, then added slowly to a large excess of water (2 liters in a 4.5
liter beaker). The solution was stirred at room temperature for 3 hr, the solid was
filtered off, washed repeatedly with water, and followed by washing with ethanol
15 (20 ml). The product was recrystallized once from THF/water and dried at 60°C in
a vacuum oven for 6 hr. to produce 50 g (79% yield) of N-propylphenyl-3-
formylcarbazole. ¹H-NMR and IR spectra confirmed the structure of the product.

Compound (9) was prepared from N-propylphenyl-3-formylcarbazole
(50 g, 0.16 mol), N-methyl-N-phenylhydrazine (20.77 g, 0.17 mol), THF (200 ml),
20 and concentrated HCl (1 ml) according to the procedure described for Compound
(2). After heating at reflux for 4 hr. and cooling to room temperature, ethanol
(100 ml) was added and the flask was stirred at room temperature overnight. The
yellowish solid was filtered off and dried in a vacuum oven at 70°C for 3 hr. The
product was recrystallized three times from isopropyl alcohol, with activated
25 charcoal used in all three recrystallizations. Celite was also used in the third
recrystallization. The product was dried in a vacuum oven at 70°C for 6 hr. to
yield 40 g (60% yield) of Compound (9). ¹H-NMR and IR spectra were in
agreement with the structure of Compound (9).

Compound (10)

30 Compound (10) was prepared from N-2-ethylhexyl-3-formylcarbazole
(26 g, 0.084 mol, prepared as described for Compound (9)),

N-methyl-N-phenylhydrazine (11 g, 0.09 mol), THF (100 ml), and concentrated HCl (1 ml) according to the procedure described for Compound (2). The product was recrystallized three times from isopropyl alcohol using activated charcoal in all three recrystallizations. Celite was also used in the third recrystallization. 20 g (57% yield) of Compound (10) were obtained. ¹H-NMR and IR spectra were in agreement with the structure of Compound (10).

Compound (11)

To a 5-liter, 3-neck round bottom flask equipped with mechanical stirrer and reflux condenser were added carbazole (360 g, 2.15 mol), 1,10-dibromodecane (300 g, 1 mol), benzyltriethyl ammonium chloride (36 g, 0.16 mol), THF (1200 ml), and 50 % aqueous solution of NaOH (720 g). The reaction mixture was heated at reflux for 5 hr., cooled to room temperature, and stirred at room temperature overnight. The product was filtered off, washed repeatedly with water, and dried in a vacuum oven at 70°C for 6 hr. to yield 432 g (91% yield) of a dimer.

To a 3-liter, 3-neck round bottom flask equipped with mechanical stirrer and addition funnel was added DMF (542 ml, 7 mol) and the flask was cooled in a salt/ice bath. When the temperature inside the flask reached 0°C, POCl₃ (652 ml, 7 mol) was slowly added using the addition funnel. The inside temperature was not allowed to rise above 5°C during the addition of the POCl₃. After the addition of POCl₃ was complete, the flask was allowed to warm to room temperature and the dimer (237 g, 0.5 mol) was added. The flask was heated at 90°C for 48 hr., cooled to room temperature, and added slowly to a large excess of water. The solid was isolated and recrystallized from THF/water to produce 150 g (59% yield) of the corresponding tetraaldehyde. ¹H-NMR and IR confirmed the structure of the tetraaldehyde.

Compound (11) was prepared from the tetraaldehyde (23.46 g, 0.04 mol), N-methyl-N-phenylhydrazine (20.52 g, 0.17 mol), THF (500 ml), and concentrated HCl (5 ml) according to the procedure described for Compound (2). The product was isolated, recrystallized 3 times from toluene using activated charcoal in all three recrystallizations. Celite was also used in the third recrystallization. 15 g

(37% yield) of Compound (11) were obtained. ¹H-NMR and IR were in agreement with the structure of Compound (11).

Compound (12)

A dimer was prepared from carbazole (35.54 g, 0.24 mol), triethylene glycol di-p-tosylate (50 g, 0.11 mol), benzyltriethyl ammonium chloride (3.77 g, 0.017 mol), toluene (200 ml), and 50% aqueous solution of NaOH (80 ml) according to the procedure described for Compound (11). 41.74 g (85% yield) of the dimer were obtained. ¹H-NMR and IR confirmed the structure of the dimer.

The corresponding tetraaldehyde was prepared from DMF (100 ml, 1.3 mol), POCl₃ (122 ml, 1.3 mol), and the dimer (41.65 g, 0.09 mol) according to the procedure described for Compound (11). 20 g (38% yield) of the tetraaldehyde were obtained. ¹H-NMR and IR confirmed the structure of the tetraaldehyde.

Compound (12) was prepared from the tetraaldehyde (11.21 g, 0.02 mol), N-methyl-N-phenylhydrazine (10.26 g, 0.084 mol), THF (300 ml), DMF (100 ml), and concentrated HCl (1 ml) according to the procedure described for Compound (11). 10 g (50% yield) of Compound (12) were obtained. ¹H-NMR and IR spectra were in agreement with the structure of Compound (12).

B. Organic Photoreceptor Belt Preparation

A charge transport solution containing a selected charge transport compound in Polycarbonate Z binder (commercially available from Mitsubishi Gas Chemical under the designation "Lupilon Z-200" resin) was prepared by combining 120.0 g of tetrahydrofuran with 15.0 g of Polycarbonate Z, 0.03 g of Dow Corning 510 Fluid. The resulting charge transport solution contained a charge transport compound:polycarbonate Z ratio of either 2:3 or 1:1 depending on the solubility of the charge transport compound. The charge transport solution was then die coated onto 3 mil (76 micrometer) thick polyethylene terephthalate (PET) film (Melinex 442 polyester film from Dupont) having a 1 ohm/square aluminum vapor coat and an additional 0.25 micrometer thick PET layer overlaying the aluminum vapor coat. The purpose of including the PET overlayer was to improve adhesion and prevent charge injection into the charge transport layer. The dried charge transport layer had a

nominal thickness of 8.75 micrometers. Die coating (also known as slot coating) techniques are described by E. Cohen and E. Guttoff, *Modern Coating and Drying Technology*, VCH Publishers, Inc. New York, 1992, pp. 117-120.

5 A dispersion was prepared by micronising 32.6 g of Progen x-form metal free phthalocyanine pigment (Zeneca Inc.), 32.6 g of S-Lec B Bx-5 polyvinyl butyral resin (Sekisui Chemical Co. Ltd.), and 684.4 g of 2/1 (v/v) methyl ethyl ketone/toluene using a horizontal sand mill operating in recirculation mode for 8 hours. This stock solution was diluted to 3.5 wt.% solids by adding 1113 g of 2/1 (v/v) methyl ethyl ketone/toluene prior to coating. The resulting dispersion was die coated onto the
10 charge transport layer and dried to form a charge generating layer having a nominal thickness of 0.27 micrometer. This dual layer organic photoconductor was then overcoated with a barrier layer.

Two different barrier layer solutions were used. The first ("Barrier A") was prepared by mixing 86.3 g of 3% Methocel A15LV in water, 86.3 g of 3% Gantrez
15 AN-169 polymer (ISP Technologies) in water, 172.44 g of methanol, 0.65 g of 40% Glyoxal 40 in water, and 0.07 g Triton X-100 surfactant following the procedure described in Ackley et al., "Organic Photoreceptors for Liquid Electrophotography," USSN 09/504,456, filed February 16, 2000 and assigned to the same assignee as the present application. The other barrier layer solution ("Barrier B") was prepared by
20 combining 217.6 g of 6% S-Lec Bx-5 polyvinyl butyral resin, 1385.7 g isopropyl alcohol, 33.5 g Nalco 1057 colloidal silica, 33.1% Z-6040 silane (Dow Corning 50/50 in isopropyl alcohol/water), and 130.17 g Gantrez AN-169 polymer following the procedure described in U.S. 5,733,698.

The barrier layer solution was die coated onto the dual layer organic
25 photoconductor and dried to form a layer having a nominal thickness of 0.4 micrometer.

C. Thermal Transitions

Thermal transition data for various charge transport materials was collected using a TA Instruments Model 2929 Differential Scanning Calorimeter (New Castle,
30 DE) equipped with a DSC refrigerated cooling system (-70°C minimum temperature limit), and dry helium and nitrogen exchange gases. The calorimeter ran on a

Thermal Analyst 2100 workstation with version 8.10B software. An empty aluminum pan was used as the reference.

Samples were tested both neat and as a mixture with Polycarbonate Z ("PCZ"). The neat samples were prepared by placing 4.0 to 8.0 mg of neat charge transport material into an aluminum sample pan and crimping the upper lid to produce a hermetically sealed sample for DSC testing. The results were normalized on a per mass basis.

The Polycarbonate Z-mixed samples were prepared by filling the bottom portion of the aluminum sample pan to capacity with a 15-20% solids solution of the charge transport material in Polycarbonate Z, followed by air-drying overnight. Each air-dried sample was then placed in a convection oven at 50-55°C for another 24-48 hours to eliminate trace solvent, after which the upper sample lid was crimped on to produce a hermetically sealed sample for DSC testing. Typical sample size was 7.0 to 15.0 mg. Again, the results were normalized on a per mass basis.

Each sample was subjected to the following protocol to evaluate its thermal transition behavior:

1. Equilibrate at 0°C (Default--Nitrogen Heat Exchange Gas);
2. Isothermal for 5 min.;
3. External Event: Nitrogen Heat Exchange Gas;
4. Ramp 10.0°C/min. to a temperature 30°C above the CTM's melting point;
5. External Event: Helium Heat Exchange Gas;
6. Isothermal for 5 min.;
7. Ramp 10.0°C/min. to 0°C;
8. External Event: Nitrogen Heat Exchange Gas;
9. Isothermal for 5 min.;
10. Ramp 10.0°C/min. to a temperature 40°C above the CTM's melting point;
11. External Event: Helium Heat Exchange Gas;
12. Isothermal for 5 min.;
13. Ramp 10.0°C/min. to 0°C;

14. External Event: Nitrogen Heat Exchange Gas;

15. Isothermal for 5 min.;

16. Ramp 10.0°C/min. to 275°C.

5 The first cycle (steps 1-7) was used to (a) remove the thermal history of the sample, (b) obtain the melting transition for crystalline charge transport materials, and (c) obtain a homogeneous charge transport material/Polycarbonate-Z mixture in the event the charge transport material crystallized during sample preparation. A homogeneous mixture is obtained only if the charge transport material (melt or cast) is miscible with the Polycarbonate-Z.

10 The second cycle (steps 8-13) was used to identify the glass transition temperature and charge transport material recrystallization or melting transitions.

The third cycle (steps 14-16) was used to report the final thermal transitions.

The results are shown below in Table 1. All temperatures are reported in °C. "CTM" refers to the charge transport material (i.e., the charge transport compound, as
15 used above). "PCZ" refers to Polycarbonate Z.

TABLE 1

CTM	NEAT CTM		CTM/PCZ	Glass Transition Temperature (T _g)
	Melting Temperature (T _m)	Glass Transition Temperature (T _g)	CTM:PCZ Ratio	
3	180	None	2:3	87
4	165	None	2:3	73
5	170	None	2:3	83
6	241	64	2:3	106
7	197	59	2:3	100
9	124	32	1:1	55
10	100-115	12	1:1	46
11	129	91	2:3	—
12	134	102	2:3	133

In general, it is desirable to maximize the glass transition temperature, while at the same time maximizing solubility in the binder, in order to minimize environmental stress cracking that can occur when the organic photoreceptor is brought into contact with organic carrier liquids used in liquid toners.

D. Photo Induced Discharge Curves (PIDC)

Organic photoreceptor belts were prepared as described above. Each belt measured 50 cm long by 8.8 cm wide and was fastened to an aluminum drum having a circumference of 50 cm. The drum rotated at a rate of 7.6 cm/min. Corona charging and discharging stations were positioned around the drum.

Each belt was charged up to 500 V, stopped under an optical probe, and then discharged using a Xenon Flash lamp (XENON 456 Micropulser, Xenon Corp. Woburn, MA). Belts that were unable to attain 500 V were charged up to the maximum attainable charge acceptance voltage. The flash generated by the micropulser passed through a 780 nm optical filter, traveled through the optical probe, and discharged the area of the belt under the probe. Data was collected at a rate of 2000 samples per second for 2 seconds, and processed using software commercially available under the trade designation LABVIEW before being downloaded to a spread sheet and graphing application. Measurements were taken at both 25°C and 40°C; the latter temperature was obtained using a heating element inside the aluminum drum.

The rate at which each charge transport layer lost its charge was determined as follows. The discharge rate at the initial maximum voltage, $t(V_i)$, was taken as the amount of time required for the initial acceptance voltage (V_i) to drop to one-half of its value. The discharge rate is proportional to the initial acceptance voltage. Therefore, to compare samples on an equal basis, the discharge rates for belts made from different charge transport materials were then normalized to values that would have been obtained if the initial belt voltage charged up to 500 V by using the equation:

$$t_{500V} = t(V_i) * (V_i/500)$$

As a first approximation, the voltage across the thin barrier layer was insignificant as compared to the much thicker charge generating and charge transport layers. This implies that the 500V drop across the sample can be attributed to the charge generating and charge transport layers, and that all samples can be compared on an equal basis.

The residual potential voltage (V_{res}), was measured 310 milliseconds after the XENON Micropulser flash. This time interval was selected because it matches a key process time in a printer during actual use. The results are shown in Table 2 for organic photoreceptors incorporating various charge transport compounds. All values for t_{500V} are reported in milliseconds. All values for V_i and V_{res} are reported in volts.

TABLE 2

CTM	Barrier	V_i @ 25°C	t_{500V} @ 25°C	V_{res} @ 25°C	V_i @ 40°C	t_{500V} @ 40°C	V_{res} @ 40°C	ratio t_{500V} 25°C/ 40°C
3	None	150	62.5	68	122	17.2	46	3.6
4	None	344	10.8	110	368	0.3	38	36.0
5	None	389	12.3	124	372	2.1	75	5.9
7	A	495	0.8	17	370	0.6	11	1.3
9	B	508	8.0	139	517	3.0	113	2.7
10	A	491	3.7	33	408	1.7	22	2.2

In general, it is desirable to minimize values of both V_{res} and t_{500} , while maximizing V_i . The data in Table 2 demonstrate that based upon these criteria, the performance of each organic photoreceptor was acceptable, and that photoreceptors based upon charge transport compounds (7) and (10) gave the best performance.

E. Mixtures of Charge Transport Compounds

Coating solutions were prepared by mixing charge transport compound (8 wt.%), Polycarbonate Z-200 (12 wt.%), tetrahydrofuran (80 wt.%), and DC 510 (0.019 wt.%), and heating the mixture with a hot air gun to ensure homogeneity.

After standing for approximately one hour, the sample equilibrated to room temperature to yield a clear, homogeneous solution. The solution was then hand coated using a wire-wound rod (Meyer Bar #36) onto a piece of aluminized PET measuring 12 inches by 8 inches to form a charge transport layer. A 0.2 micron thick polyester adhesion layer was applied to the aluminum side of the sheet prior to coating. Immediately following coating, the sample was dried in a oven at 80°C for 5 minutes, and then at 100°C for 2 minutes. A metal-free phthalocyanine charge generating layer was then laminated onto the dried charge transport layer to produce the organic photoconductor.

Electrostatic testing of each sample was performed and recorded on a QEA PDT-2000 instrument at room temperature. Table 3 lists the schedule of events per cycle and the appropriate definitions for this particular test procedure.

TABLE 3

Event	Measured Voltage	Time (sec)	Definition	Definition
Cycle Start	V_0	0.00	Charge Acceptance Voltage	$V_{acc}=V_0$
PreExpose	V_1	1.00	Dark Decay	$V_{dd}=V_0-V_1$
Expose Start	V_2	1.00		
Expose End	V_3	1.05	Initial Discharge Rate	$I_{dr}=(V_2-V_3)/0.05$ sec
PreErase	V_4	2.05	Contrast Voltage	$V_{cont}=V_1-V_4$
Erase	V_5	2.05		
Cycle End	V_6	3.00	Residual Voltage	$V_{res}=V_6$

For each charge-discharge cycle, the sample, which was adhered to the instrument drum, was charged up using a positive corona grid and the voltage recorded as the charge acceptance voltage (V_{acc}). After 1 second, the sample was discharged by an external, 780 nm pass-band filtered, tungsten light source that was connected to the instrument via a fiber optic cable. Each sample was exposed to 2 $\mu\text{J}/\text{cm}^2$ of energy for 0.05 sec. at a total exposure intensity of 20 $\mu\text{W}/\text{cm}^2$. The drop in voltage during the first second after charging, but before light exposure, was recorded as the dark decay value for the sample (V_{dd}).

The drop in voltage during the 0.05 sec. exposure to the 780 nm imaging light was recorded as the initial discharge rate for the sample. The contrast voltage (V_{cont}) was obtained prior to the sample being completely erased (1 second before exposure end). The residual voltage (V_{res}) was recorded 0.95 sec. after erasure.

5 The sample was then recharged for the beginning of the next cycle. Table 4 summarizes the average values obtained over 100 cycles.

TABLE 4

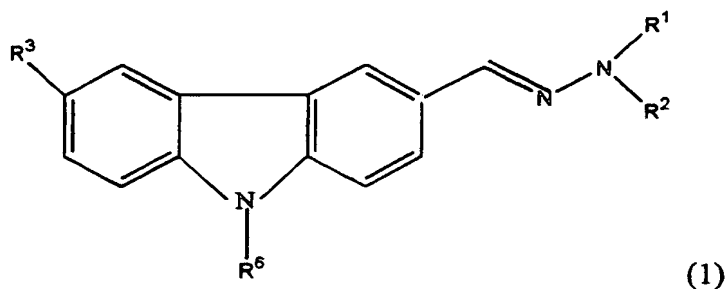
CTM	V_{acc} (volts)	V_{dd} (volts)	V_{cont} (volts)	V_{res} (volts)
7	455	158	223	78
3	583	86	378	97
4	386	59	148	76
5	506	73	338	77
7+3 (1:1)	610	159	392	48
7+4 (1:1)	616	124	446	37
7+5 (1:1)	588	142	357	42

10 In general, it is desirable to maximize V_{acc} and V_{cont} , while minimizing V_{res} and V_{dd} . The data in Table 4 demonstrate that, while the performance of each organophotoreceptor was acceptable, mixtures of charge transport compounds performed even better than the individual charge transport compounds alone.

15 All patents, patent applications, and publications disclosed herein are incorporated by reference in their entirety, as if individually incorporated. The foregoing detailed description and examples have been given for clarity of understanding only. No unnecessary limitations are to be understood therefrom. The invention is not limited to the details shown and described, for variations
20 obvious to one skilled in the art will be included within the invention defined by the claims.

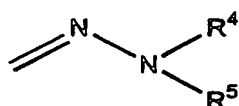
WHAT IS CLAIMED IS:

1. A charge transport compound having the formula:



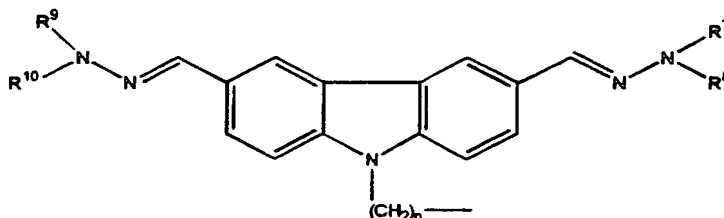
where R^1 and R^2 , independently, are hydrogen, an alkyl group, or an
 5 aryl group;

R^3 is hydrogen or a hydrazone group having the formula



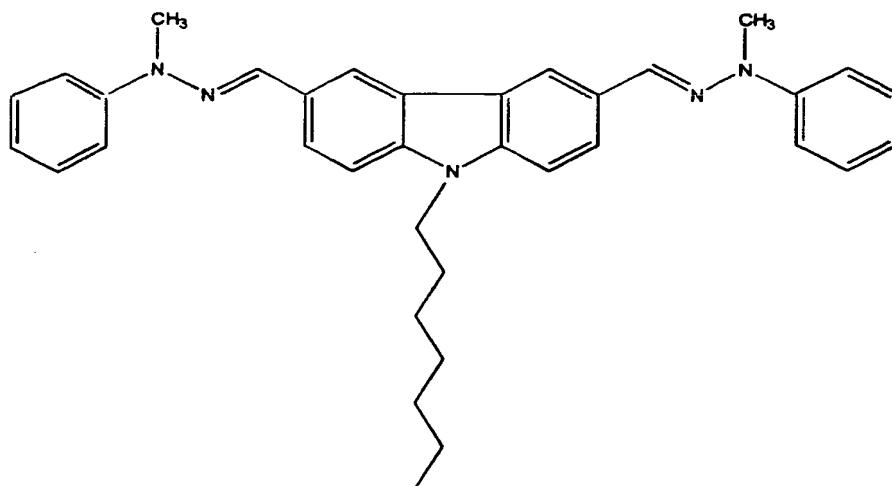
R^4 and R^5 , independently, are hydrogen, an alkyl group, or an aryl
 group;

10 R^6 is an aryl group; a straight or branched alkyl group having at
 least 7 carbon atoms; a group having the formula $-(CH_2)_n-Ar$ where n is at least 3,
 Ar represents an aryl group, and one or methylene groups is optionally substituted
 with a heteroatom; or a carbazole group having the formula



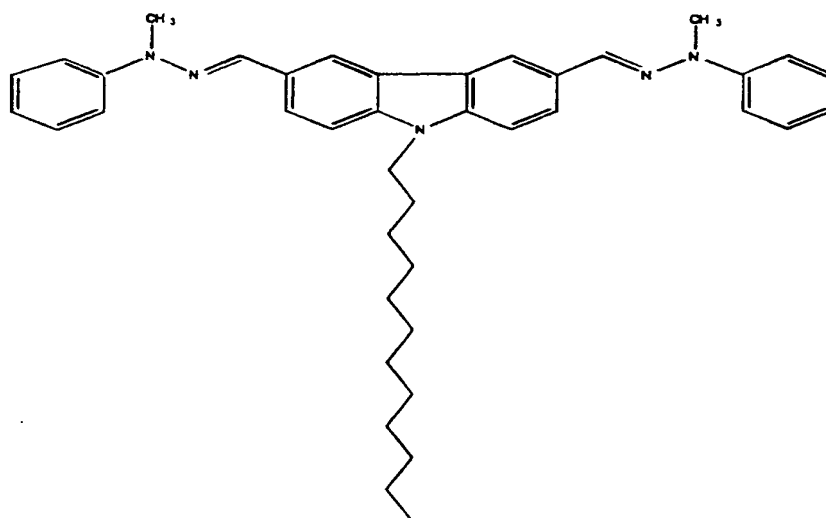
where R^7 , R^8 , R^9 , and R^{10} , independently, are hydrogen, an alkyl group, or an aryl group, n is at least 3; and one or methylene groups is optionally substituted with a heteroatom.

- 5 2. An organic photoreceptor comprising:
- (a) a charge transport compound according to claim 1;
- (b) a charge generating compound; and
- (c) an electroconductive substrate.
3. An organic photoreceptor according to claim 2 wherein said organic
- 10 photoreceptor is in the form of a flexible belt.
4. An organic photoreceptor according to claims 2 and 3 comprising:
- (a) a charge transport layer comprising at least one of said
- charge transport compounds and a polymeric binder;
- (b) a charge generating layer comprising said charge generating
- 15 compound and a polymeric binder; and
- (c) said electroconducting substrate.
5. An organic photoreceptor according to claims 2-4 wherein said charge
- transport layer comprises two of said charge transport compounds in a ratio with one
- another of about 9:1 to about 1:1.
- 20 6. An organic photoreceptor according to claims 2-5 wherein said charge
- transport layer is intermediate said charge generating layer and said electroconductive
- substrate.
7. An organic photoreceptor according to claims 2-6 wherein R^3 is a
- hydrazone group, R^4 is a methyl group, and R^5 is a phenyl group.
- 25 8. An organic photoreceptor according to claims 2-7 wherein said charge
- transport compound is selected from the group consisting of



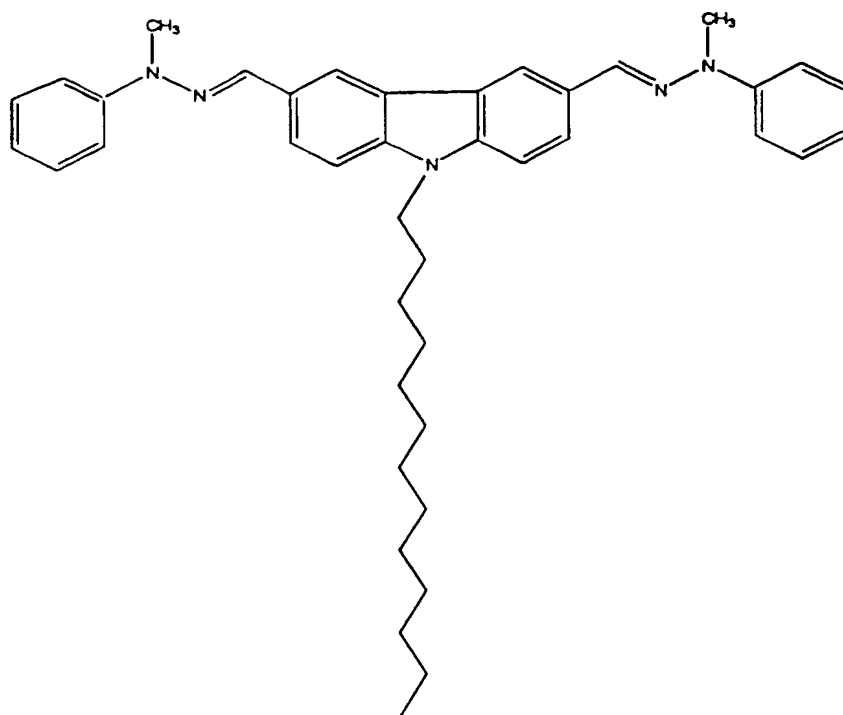
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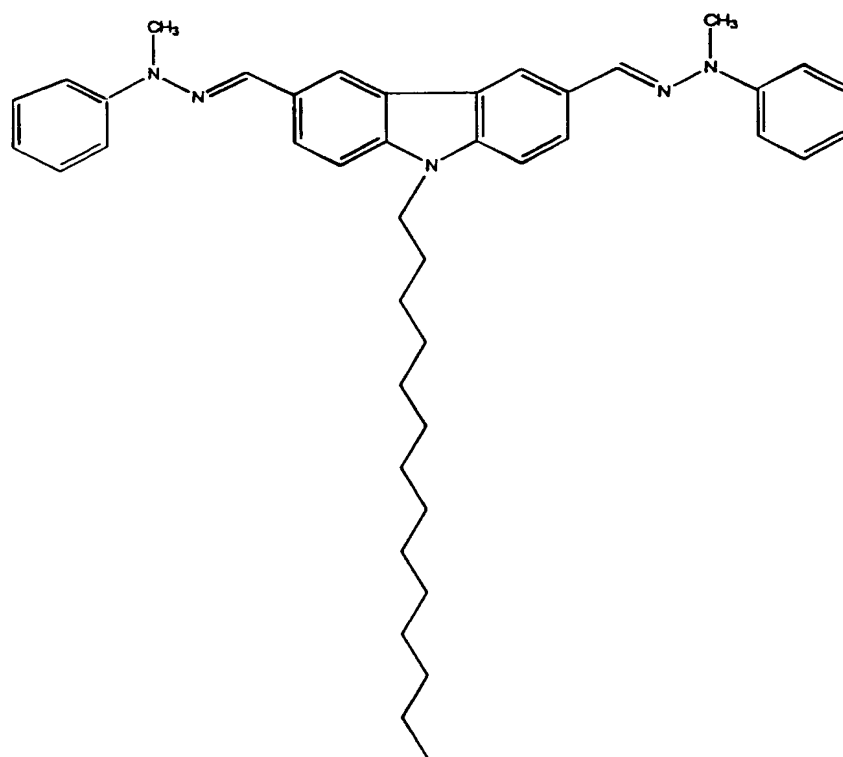


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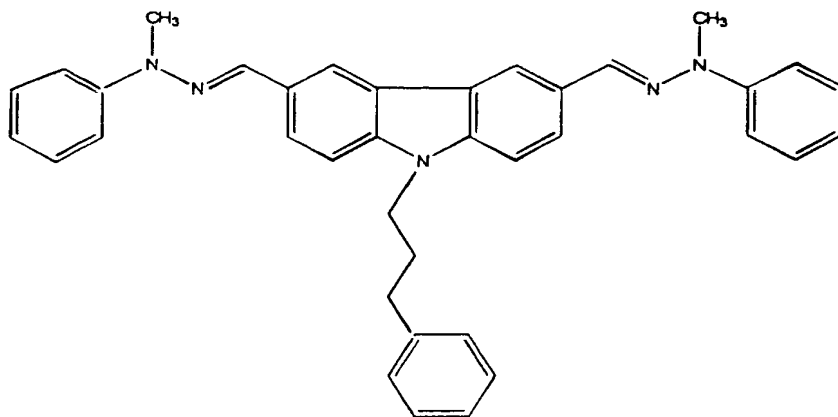
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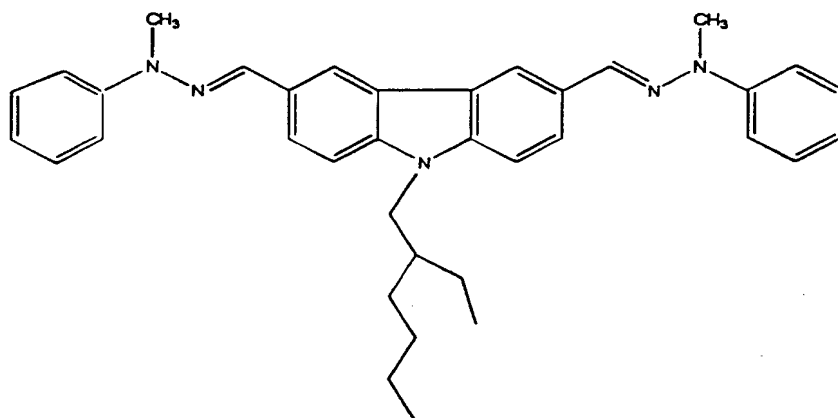
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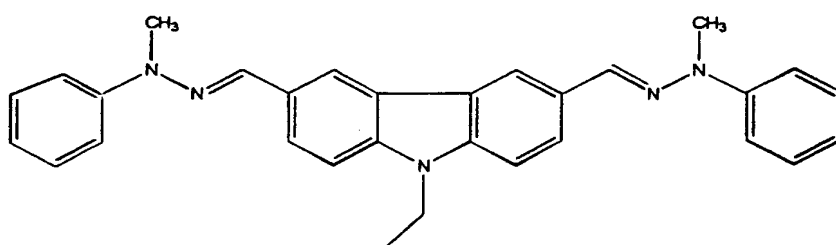
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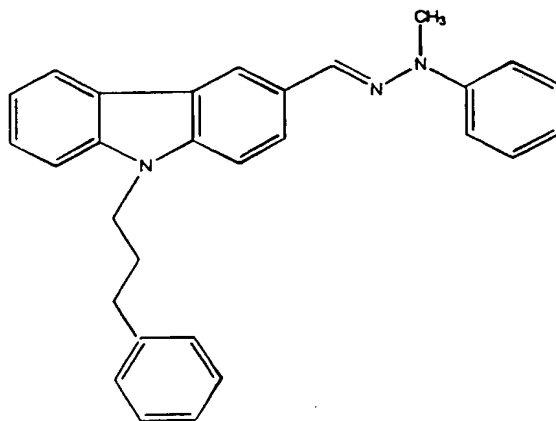
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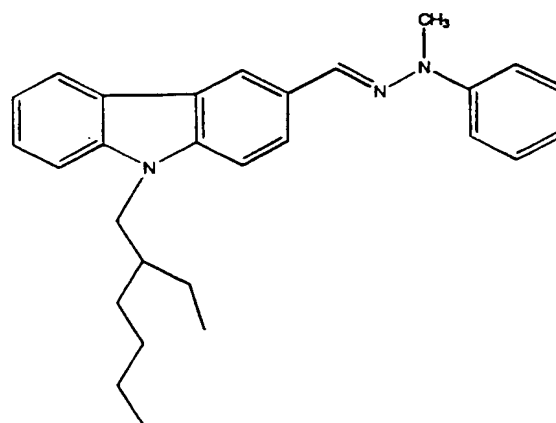
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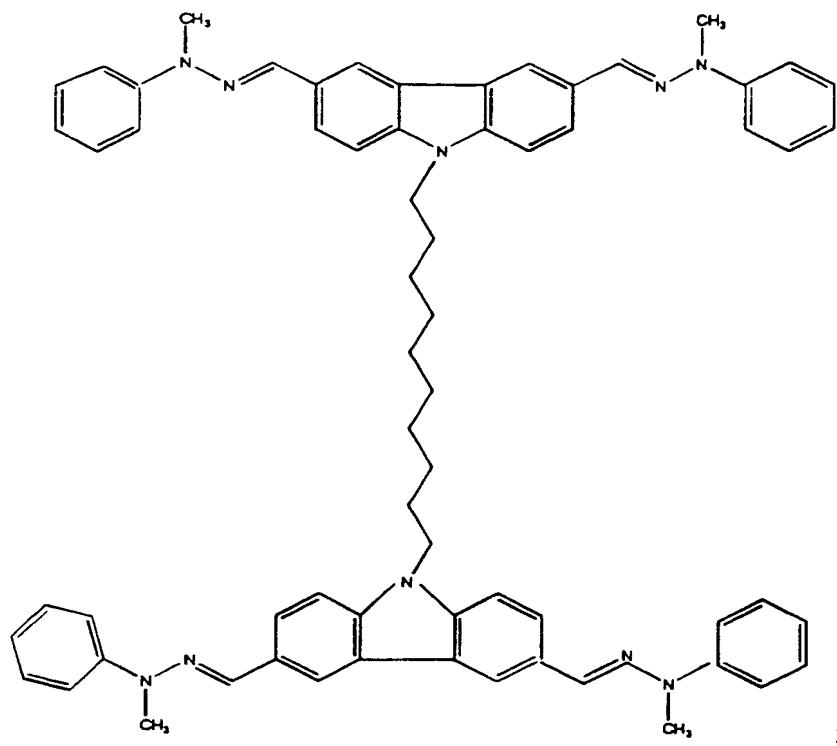
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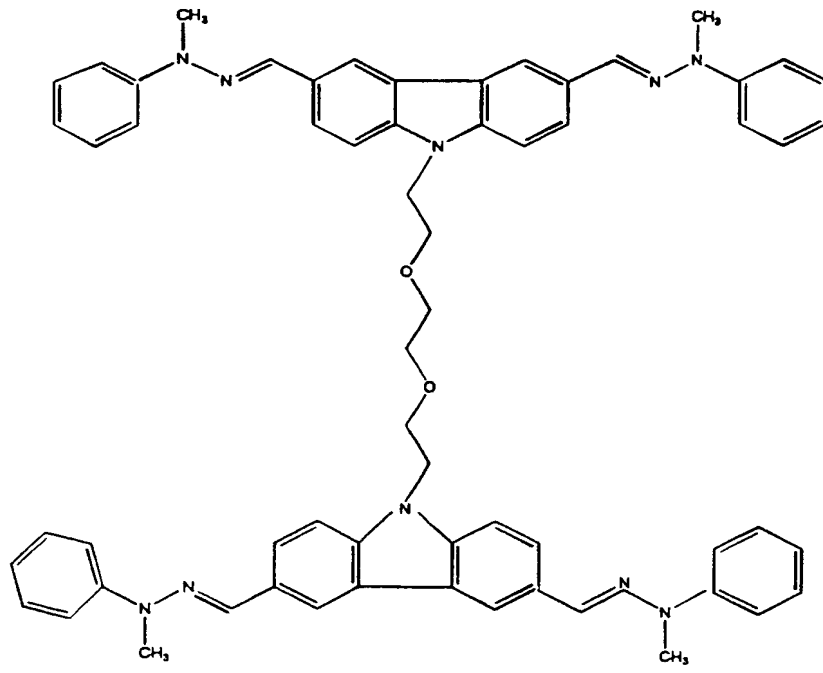
(9)



(10)



(11)



(12)

and combinations thereof.

9. An electrophotographic imaging apparatus comprising:
- (a) a plurality of support rollers; and
 - (b) an organic photoreceptor in the form of a flexible belt
- 5 supported by said support rollers,
- said organic photoreceptor comprising:
- (i) a charge transport compound according to claims 2-8;
 - (ii) a charge generating compound; and
 - (iii) an electroconductive substrate.
- 10 10. An electrophotographic imaging process comprising:
- (a) applying an electrical charge to a surface of an organic photoreceptor comprising:
- (i) a charge transport compound according to claims 2-8;
 - (ii) a charge generating compound; and
 - (iii) an electroconductive substrate;
- 15 (b) imagewise exposing said surface of said organic photoreceptor to radiation to dissipate charge in selected areas and thereby form a pattern of charged and discharged areas on said surface;
- (c) contacting said surface with a liquid toner comprising a dispersion of colorant particles in an organic liquid to create a toned image; and
 - (d) transferring said toned image to a substrate.
- 20

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/21553

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 G03G5/06 C07D209/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G03G C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 988 596 A (UEDA HIDEAKI) 29 January 1991 (1991-01-29) column 43 -column 44; examples IV-29 claims 1,3; figures 1-5 ---	1,2,4,6, 9,10
X	PATENT ABSTRACTS OF JAPAN vol. 011, no. 337 (P-633), 5 November 1987 (1987-11-05) & JP 62 121460 A (KONISHIROKU PHOTO IND CO LTD), 2 June 1987 (1987-06-02) abstract ---	1,2,4,9, 10
P,X	WO 00 22483 A (IMATION CORP) 20 April 2000 (2000-04-20) claims 1-10 --- -/--	1-4,9,10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"&" document member of the same patent family

Date of the actual completion of the international search

13 October 2000

Date of mailing of the international search report

24/10/2000

Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

International Application No

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